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From sandwich and triple-decker to organometallic polymers

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ABSTRACT. Several types of organometallic polymers with different backbones are known. Our approach for the construction of metal-containing polymers uses the ability of Lewis-acidic boron heterocycles to interact antifacially with metals. The boron heterocycle 2,3-dihydro-1,3-diborole (*10*) not only allows the formation of sandwich and triple-decker complexes but also the stacking of metal complex fragments to oligodecker and polydecker compounds. This account reviews sandwich and triple-decker complexes as potential building blocks for polymers, and reports on the nickel- and rhodium-2,3-dihydro-1,3-diborolyl polymers *79* and *80*.

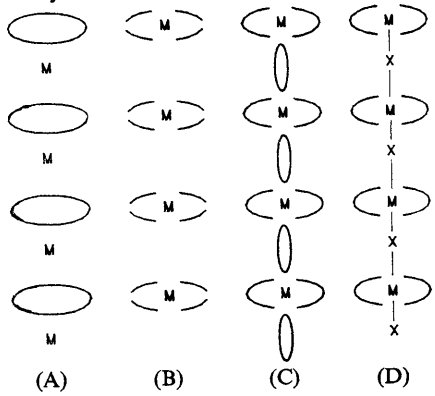
The bibliography contains 46 references.

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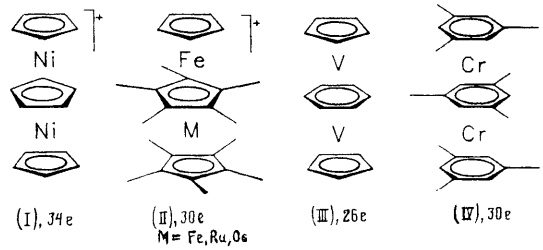
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I. Introduction

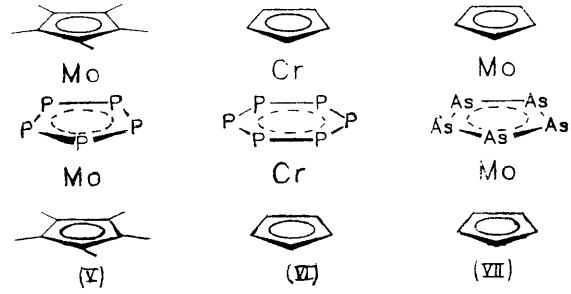
Organometallic polymers may be divided into several classes, depending on the backbone of the polymers. In coordination polymers of type *B*, e.g. in tetracyanoplatinate complexes $M_2Pt(CN)_4$ [1] and in porphyrinmetal complexes[2] the metals have direct contact via the d_{z^2} orbitals. Other polymers may contain heterocycles (type *C*) or chalcogen and halogen atoms (type *D*) as bridging ligands between the metal atoms.[3] Our approach for the construction of organometallic polymers uses electron-poor boron heterocycles in bridging positions (type *A*). They allow antifacial coordination with strong metal-ligand interactions in oligodecker and polydecker sandwich complexes.[4,5] A theoretical study of stacking complex fragments to one-dimensional arrangements has been published by Böhm.[6]



The idea of synthesising polydecker sandwich compounds (stacked cyclic ligands with metal atoms in between) is as old as metallocene chemistry. Early information on triple-decker sandwich species came from mass-spectroscopic studies of ferrocene and nickelocene. Parent ions like $Cp_3Ni_2^+$, Cp_3NiFe^+ and $Cp_3Fe_2^+$ have been detected.[7] It was two decades after the mile-stone discovery of ferrocene when Werner and Salzer[8] obtained the first triple-decker sandwich $Cp_3Ni_2^+BF_4^-$ (*1*) from Cp_2Ni and HBF_4. Only recently the long-sought complexes *2* with M = Fe, Ru, Os; M′ = Fe, Os were synthesised by Rybinskaya, Kudinov, et al.[9] Dinuclear complexes of the types *3* and *4* with arenes in bridging position have been reported by Jonas[10] and Lamanna.[11]



The chemistry of triple-deckers with homocyclic bridging ligands experienced a most interesting addition when Scherer, et al.[12] prepared the first dinuclear compounds *5* and *6* with μ-P_5 and μ-P_6 rings. Another example is the triple-decker *7* with an asymmetric As_5-ring.[13]



Until now all attempts to obtain larger molecules with carbocyclic ligands in bridging positions have failed. In contrast to these findings organoboron heterocycles have not only allowed the construction of a large number of triple-decker complexes, but also the first tetra-, penta- and hexadecker, as well as polydecker sandwich complexes.[4,5] Several reviews have summarised the extensive chemistry of boron heterocycles as ligands in transition metal complexes.[14–16]

In order to outline the principles for the construction of oligo- and polydecker complexes it is necessary to refer to the electronic situation (HOMO/LUMO) of triple-decker complexes as published by Hoffmann, et al.[17] and by Chesky and Hall.[18] *1* has 34 valence

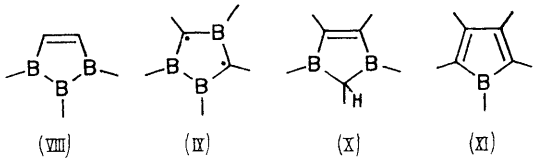
electrons (Ve, closed shell). In *2*, 30 VE (closed shell) are present. The diamagnetic triple-decker cations *2* are the electronic analogues of ferrocene (18 VE), while *1* is that of nickelocene (20 VE). They are formed when the sandwich complexes are stacked with a CpM^+ moiety. Applying the electron-counting for triple-decker to oligodecker complexes, we proposed that the optimum number of valence electrons is given by $12n + 6$, where n is the number of stacking units, each composed of a cyclic ligand and a metal (ferrocene, $n = 1$, 18 VE; *2*, $n = 2$, 30 VE), for $n = 3$ and 4 the optimum numbers are 42 and 54 VE. The maximum VE number should be given by $14n + 6$; examples are Cp_2Ni ($n = 1$, 20 VE) and *1* ($n = 2$, 34 VE). However, 48 VE for tetradecker ($n = 3$) has not yet been verified.

To date the smallest VE number for a triple-decker is observed in *3* (26 VE) belonging to the series with $10n + 6$ VE. On this basis we expect 36 VE as a minimum number for tetradecker complexes ($n = 3$).

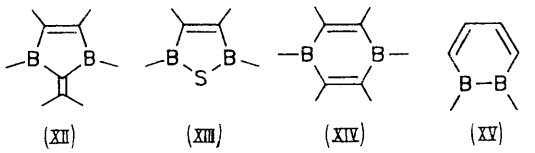
For the design of oligodecker complexes one should focus the synthetic efforts at or near $12n + 6$ VE species, since chances for the realisation of such species are greatest. If we assume that $12n + 6$ species have a closed shell arrangement, then $11n + 6$ VE species have a hole (11 VE), and $13n + 6$ VE have an extra electron (13 VE) per stacking unit. Both should lead to a half filled band in a polydecker arrangement.

II. Boron heterocycles as ligands[14–16,19,20]

The organic ligands C_5H_5 and C_6H_6 in bridging positions yield complexes with weak interactions between metals and the μ-ligands. This is well documented by the high reactivities of *1–4*. Replacements of CH groups in carbocyclic ligands by BH or BR increase the acceptor properties of the μ-ligands, and thereby strengthen the antifacial interactions to the neighbouring metals. The following boron heterocycles *8–15*, formally derived from cyclopentadiene, fulvene, thiophene, and benzene, have been incorporated as bridging units in various types of complexes.



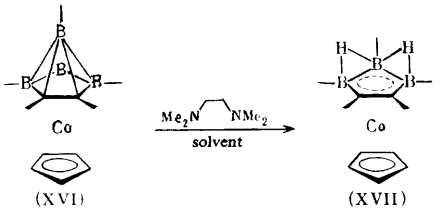
(VIII) (IX) (X) (XI)



(XII) (XIII) (XIV) (XV)

The ligands *8–10* and *15* have no independent stability. They are formed during complexation via activation of B–H or C–H bonds by the metal centre leading to the elimination of hydrogen. *8* and *9* function as 2e donors, *10* as a 3e donor and *11–15* supply 4e for bonding to one or two metal moieties.

Because of its low donor potential, *8* cannot be stabilised in sandwich complexes unless two more hydrogens are incorporated into the C_2B_3 framework. An example is *17*, obtained by the "decapitation" of the sandwich *16* (alternatively described as a *closo* metallo-carborane) with tetramethylethylenediamine. In *17* the two bridging hydrogens function as 2e donors, as does the apex BH group in *16*.[14,20]



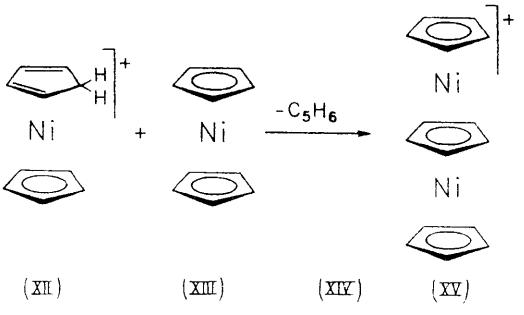
(XVI) (XVII)

The ligands *10–14* have been used to synthesise various sandwich compounds having good acceptor functions to allow the formation of triple-decker complexes.

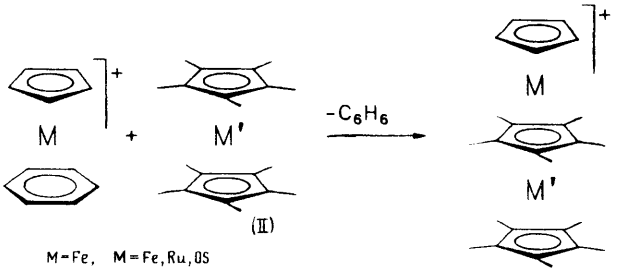
III. Triple-decker complexes

1. Homocyclic ligands in triple-decker complexes

Protonation of nickelocene, with HBF_4 at low temperature occurs at the C_5H_5 ring to give the 18 VE species. This then loses C_5H_6 and the resulting $(C_5H_5)Ni^+$ quantitatively stacks nickelocene to give *1*.[8] A related approach has been used to obtain the diamagnetic species *2* by replacing benzene in $[(C_6H_6)M(C_5H_5)]^+$ complexes with a sandwich molecule.[9] The formation of *3* occurs when $(C_3H_5)V(C_3H_5)_2$ reacts with cyclohexadiene, leading to the $(C_5H_5)V(C_6H_6)$ intermediate, which is stacked to yield *3*.[10]

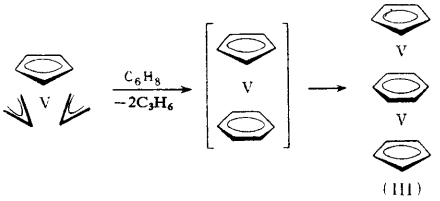


(XII) (XIII) (XIV) (XV)



(II)

M=Fe, M=Fe,Ru,OS



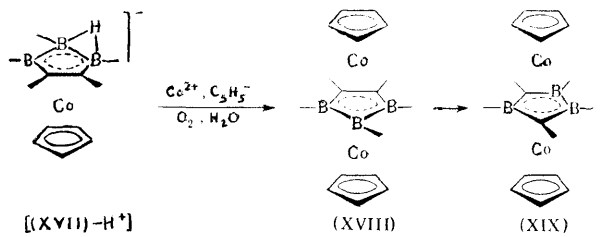
(III)

The formation of *4* via co-condensation of mesitylene and chromium atoms also occurs via stacking of the bis(mesitylene)-chromium with a $Cr(C_6H_3Me_3)$ moiety.[11]

In contrast the triple-deckers *5* and *7* are built from dinuclear species and P_4 molecules, which requires the formation of the P_n ring at the metal centres. A detailed study of *6* has been published.[12]

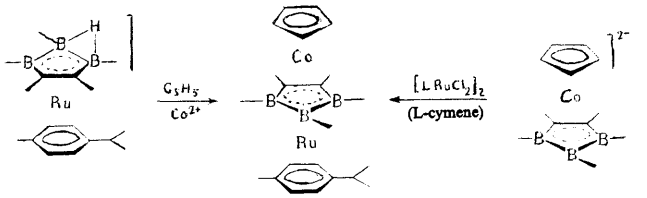
2. The isomeric μ-$R_2C_2B_3H_3$ ligands *8* and *9*

The synthesis of the first neutral triple-decker sandwich complex *18* has been achieved by Grimes et al.[21] via a three-component reaction of $R_2C_2B_4H_5^-$, Co^{2+} and $C_5H_5^-$, followed by treatment of the reaction mixture with oxygen and water. The sandwich *17* plays the key-role in the stacking reaction leading to *18* in a low yield. A designed synthesis involves a deprotonation of *17* to give [*17*−H^+], which is then reacted with $Co^{2+}/C_5H_5^-$.



[(XVII)−H^+] (XVIII) (XIX)

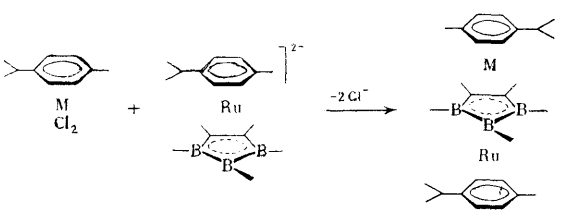
The red complex *18* (30 VE) quantitative isomerises at 400 °C to give the green 2,4-isomer *19*. Replacing one cobalt atom in *18* by iron leads to a paramagnetic 29 VE species. It is obtained in 20% yield by deprotonation of $(Et_2C_2B_3H_5)Fe(C_8H_{10})$ with NaH followed by reaction with $CoCl_2$ and $C_5H_5Na^+$.[22] For the synthesis of *20* a similar strategy has been applied. *20* is obtained in 40% yield by reacting the Ru sandwich anion [*21*−H^+] with Co^{2+} and $C_5H^-_5$ or by reacting the dianion [*17*−$2H^+$] with $[(cymene)RuCl_2]_2$. In addition the analogous compound *20* with Co and Os has been prepared.



[(XXI)−H^+] (XX) [(XVII)−$2H^+$]

$[(Cymene)MCl_2]_2$ (*22*) and the dianion [*21*−$2H^+$] form the dark orange *23* and yellow *24* in 30−45% yield, respectively. Both complexes have 30 VE.

The results described above prove that for the construction of triple-decker sandwich complexes the sandwich *17* and its anions [*17*−H^+] and [*17*−$2H^+$] as well as *21* and [*21*−H^+] are the best choices to obtain dinuclear species.

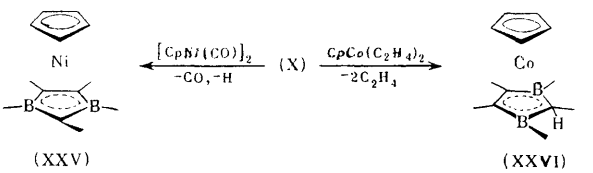


(XXII) [(XXI)−$2H^+$] (XXIII), (XXIV)

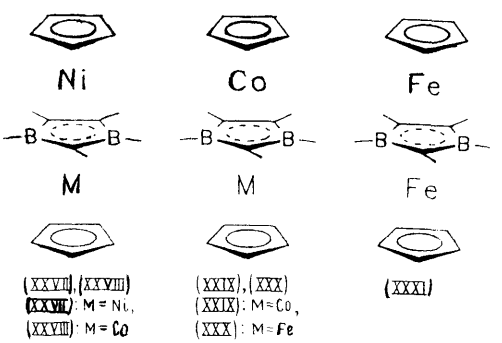
(XXIII): M=Ru, (XXIV): M=Os

3. 2,3-Dihydro-1,3-diborole complexes.[4,5,15,19,23]

2,3-Dihydro-1,3-diboroles *10* can function as 3e or 4e donors, depending on the electronic requirement of the $(C_5H_5)M$ moiety. During the formation of yellow-orange *25* a hydrogen atom is lost, whereas in the orange-red cobalt complexes *26* the ligand *10* remains intact and functions as a 4e donor through its C=C and axial C−H group. Both sandwich complexes possess high acceptor properties and they are easily stacked in high yields to give the first complete series of triple-decker sandwich complexes *27*−*31*.[25]



(XXV) (XXVI)

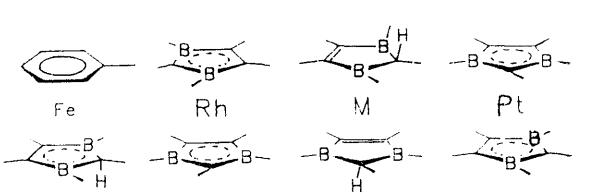


(XXVII), (XXVIII) (XXVII): M=Ni, (XXVIII): M=Co

(XXIX), (XXX) (XXIX): M=Co, (XXX): M=Fe

(XXXI)

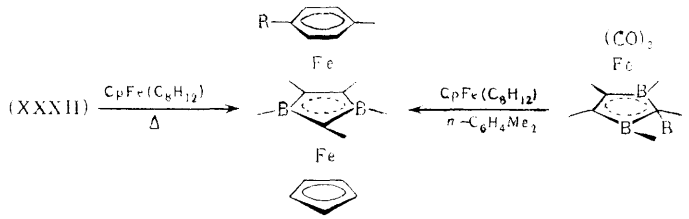
1,3-Dihydro-1,3-diborafulvene derivatives *12*[24] react with Cp_2Ni to give derivatives to *27* with C_5H_5 at the exocyclic C_6 atom. The mixed-valence blue triple-decker *31* is obtained from *10* and $[CpFe(CO)_2]_2$. A three-component reaction between *10*, $CpCo(CO)_2$ and $[CpFe(CO)_2]_2$ only leads in small yields to *30*. Deprotonation of *26* with potassium affords the anion [*26*−H^+], which on reaction with $CpFe(CO)_2I$ gives only a low yield of *30*, since a redox reaction with formation of $[CpFe(CO)_2]_2$ is favoured over the substitution of CO. The magnetic properties of *27*−*31* are in agreement with the number of unpaired electrons as derived from the MO scheme. *27*$^-$ and *30*, are diamagnetic closed-shell species.[25] The former is obtained by reduction of *27* with potassium. Several other sandwich complexes such as *32*−*36* with the 2,3-dihydro-1,3-diborole ligand have been prepared and used as precursors for triple-deckers.[5] *32* is stacked with $CpFe(C_8H_{12})$ to give the 30 VE species *37* (R=H). Another derivative of *37* ($R=CH_3$) is obtained when *38* reacts with $CpFe(C_8H_{12})$ in *p*-xylene.



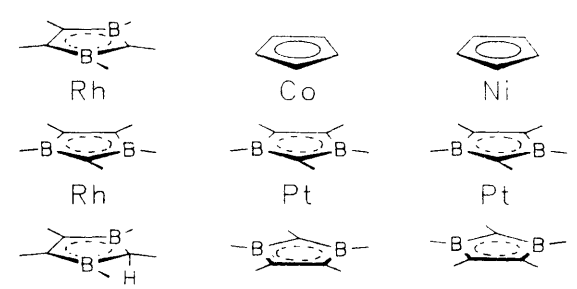
(XXXII) (XXXIII) (XXXIV), (XXXV) (XXXVI)

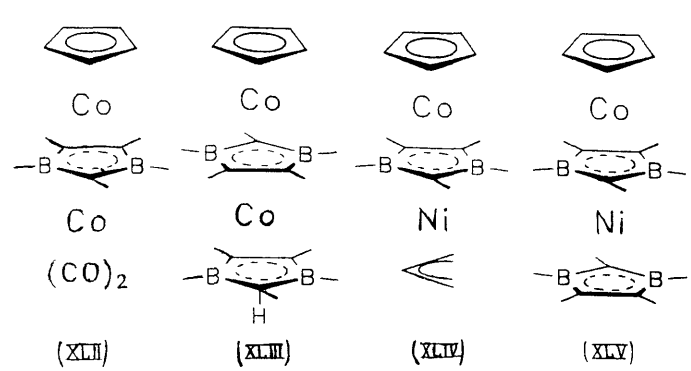
(XXXIV): M=Ni; (XXXV): M=Pt

On heating the 16 VE sandwich *33* above its melting point, an unusual condensation reaction occurs with elimination of one 2,3-dihydro-1,3-diborole ligand. Red *33* turns into green *39*, a diamagnetic 28 VE triple-decker sandwich.[26] As observed in the sandwich compounds *26*, *32*, *34*, and *35* the axial hydrogen at C2 of the dihydro-diborole ligand of *39* exhibits a high-field ^{1}H NMR signal (δ = 10.1).



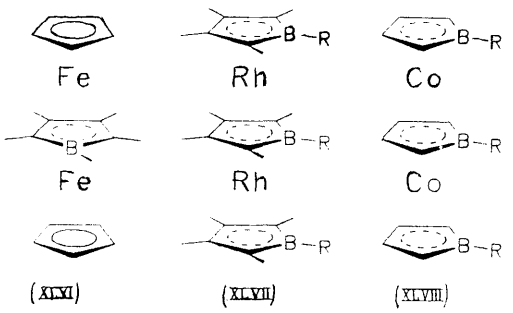
The platinum sandwich *36*, which is formed from *35* by thermal elimination of hydrogen, reacts with $CpCo(C_2H_4)_2$ and $[CpNi(CO)]_2$ to yield the unsymmetrical triple-decker sandwich complexes *40* and *41*, respectively.[27] Two further complexes of this type are obtained when *42* and *44* react with *10* to give *43* and *45*, respectively. Both are 30 VE diamagnetic species which have been used for the construction of penta- and hexadecker sandwich complexes.[29,29]





4. Triple-decker complexes with borole ligands[16]

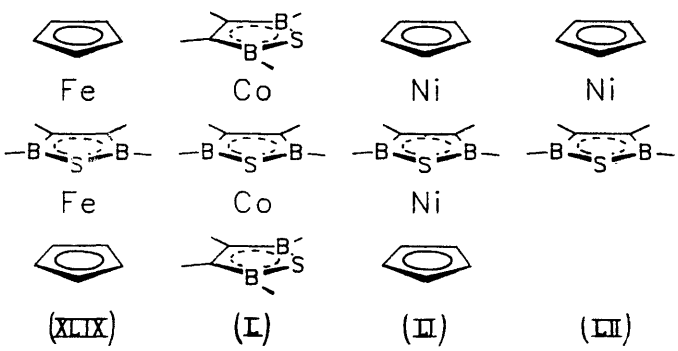
The borole ligand *11* functions as a 4e donor and a 2e acceptor to complete a η^6-system. A number of 18 VE metal complexes of *11* are known, and stacking of sandwich complexes analogous to that of *25* have been reported. Reaction of $[CpFe(CO)_2]_2$ with *11* leads to *46*, a diamagnetic 30 VE complex.



Dehydrogenative complexation of borolenes C_4H_6BR (R = Me, Ph) with $[Rh(C_2H_4)_2Cl]_2$ gives the 30 VE triple-decker *47*.[30] Its reaction with C_5H_5.Na leads to $(C_5H_5)Rh(C_4H_4BR)$ and $[(C_4H_4BR)_2Rh^+]Na^+$. $Co_2(CO)_8$ and the borole ligand form the dinuclear complex $[(C_4H_4BR)Co(CO)_2]_2$, which on thermal treatment results in the formation of *48* (R = Me). The borole rings in *48* are nearly coplanar with torsional angles of 59.8° and 72.2°.

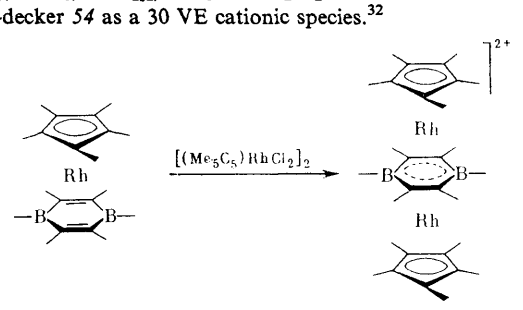
5. Triple-decker complexes with 2.5-dihydro-1,2,5-thiadiborole ligands[15]

The heterocycle *13* [31] allows the formation of various complexes, however none of the mononuclear species could be stacked to a triple-decker. *13* reacts with $[CpFe(CO)_2]_2$ and $Co_2(CO)_8$ to give the triple-decker sandwich complexes *49* and *50*. Attempts to obtain the 34 VE complex *51* only led to the paramagnetic sandwich *52*, which decomposes at 100 °C to Cp_2Ni and $(13)_2Ni$.

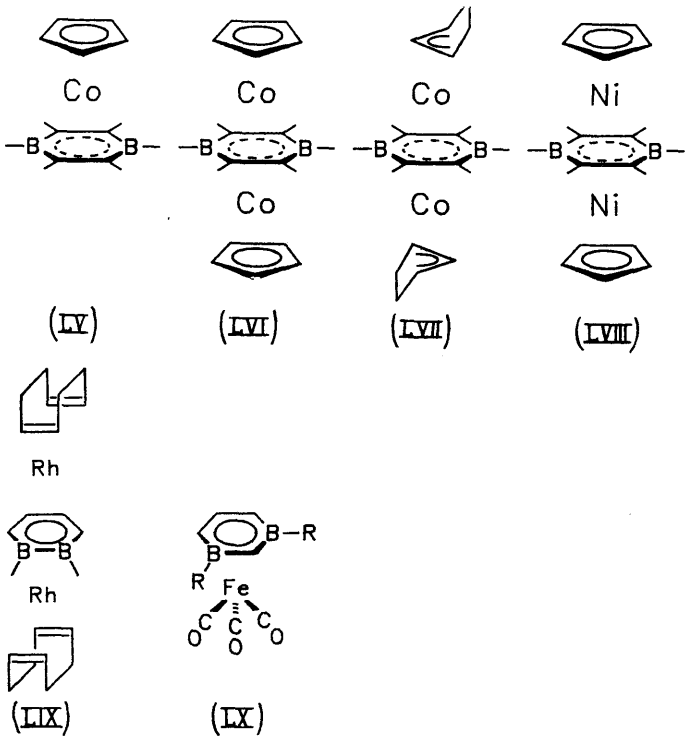


6. 1,4-Diboracyclohexadiene triple-decker complexes[16]

The 1,4-diboracyclohexadiene ligand *14* is related to the borole ligand *11* in its donor properties, and to the 2,3-dihydro-1,3-diborolyl in its acceptor properties. Treating the sandwich *53* with $[(Me_5C_5)RhCl_2]_2/AlCl_3$ in CH_2Cl_2 leads to the formation of the triple-decker *54* as a 30 VE cationic species.[32]



For the construction of the triple-deckers *56*–*58* alkyl derivatives of the 1,4-diboracyclohexene ring have been used. Dehydrogenative complexations of $C_4B_2R_4H_4$ with $(C_5H_5)Co(C_2H_4)_2$ and $[(C_5H_5)Ni(CO)]_2$ lead to the complexes *55*–*58*.[5,33,34]



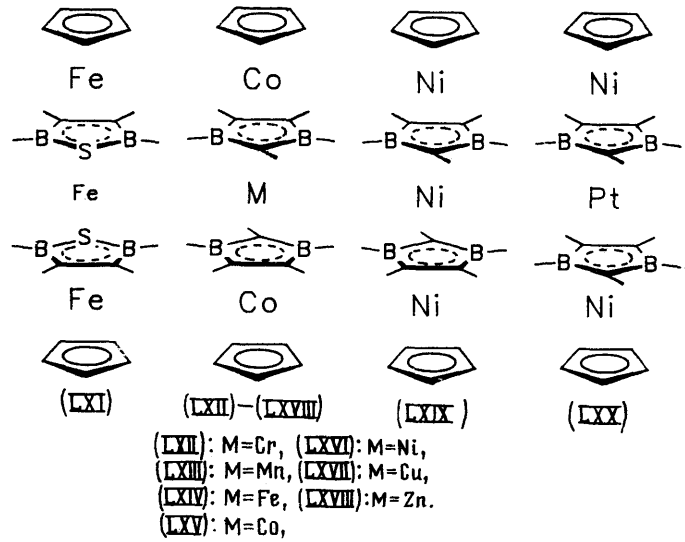
56 and *58* have 32 and 34 VE, respectively. *57* is a remarkable case, as the hydrogen atoms of $C_4B_2R_4H_6$ are transferred to the cyclopentadienyl groups to form the cyclopentenyl ligands. The constitutions of *57* and *58* have been studied by X-ray structure analyses.

7. 1-2-$B_2C_4R_6$ and 1,3-$B_2C_4R_6$ ligands

Herberich, et al.[35,36] have obtained the first examples of the title ligands stabilised in metal complexes such as *59* and *60*.

Both boron ligands in *59* and *60* should be capable of bridging two $(CH)_nM$ moieties to yield triple-decker sandwich complexes.

reaction between $[(C_5H_5Fe(COD)]_2Zn$ [38] and *13* leads to the 46 VE tetradecker $[(C_5H_5)Fe(13)]_2Zn$, which after reductive cleavage and reaction with Fe^{2+} yields the 42 VE tetradecker sandwich *61*.



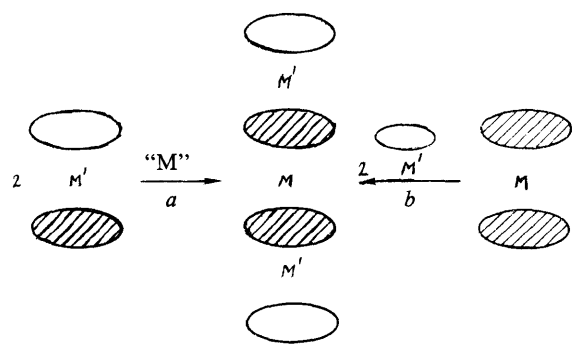


Figure 1. Routes of formation for oligodecker compounds.

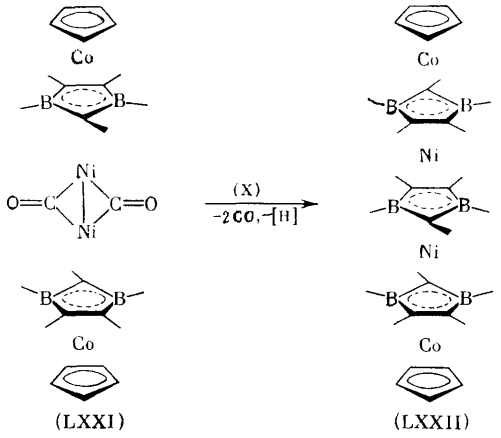
IV. Oligodecker complexes[4,5]

As outlined above the formation of triple-decker compounds can be achieved via several routes. For the construction of oligodecker complexes two reaction principles have been applied: a) reaction of two sandwich anions with a metal cation and b) stacking of a Lewis-acidic sandwich with two $(C_5H_5)M^+$ complex fragments (Fig. 1).

We synthesised and structurally characterised the first example of a tetradecker complex with the 1,2,5-thiadiborole ligand *13* in the bridging position. The diamagnetic, 42 VE hexacarbonyl dimanganese-iron complex $[(CO)_3Mn(C_2H_2B_2R_2S)]_2Fe$ was obtained in low yield by cleaving the triple-decker $[(CO)_3Mn]_2(13)$ with $C_5H_5^-$ and reacting the formed anion $[(CO)_3Mn(13)]^-$ with Fe^{2+}.[37] The

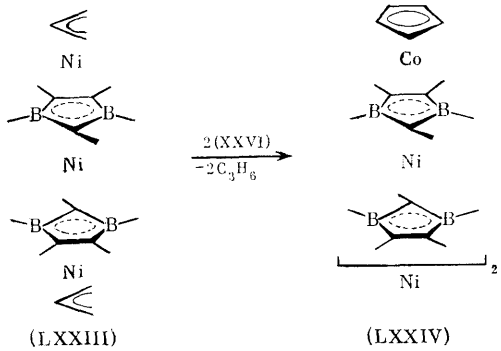
The first series of tetradecker complexes has been obtained from the deprotonated cobalt sandwich $[26-H^+]$ and the metal dications Cr(*62*), Mn(*63*), Fe(*64*), Co(*65*), Ni(*66*), Cu(*67*), and Zn(*68*).[39,40] With the exception of *68* (M = Zn) the highly coloured trinuclear species are paramagnetic; the compounds *62*–*65* have a high-spin configuration. All complexes are structurally characterised: the 2,3-dihydro-1,3-diborolyl rings adopt an antiperiplanar arrangement, and the central metal to ring distances correlate well with the Shannon–Prewitt ionic radii for octahedrally coordinated M^{2+} ions. Considerable deviations from the ideal tetradecker sandwich structure are observed due to a slip of the central metal away from the position above the centroid of the heterocycle towards the C2 carbon (between the two boron atoms). In contrast to the antiperiplanar arrangement of the boron heterocycles in the

diamagnetic 46 VE tetradecker *69*,[4] the isoelectronic platinum complex *70*,[27] obtained via reaction type *b*) in Fig. 1, exhibits a synclinal conformation.



(LXXI) (LXXII)

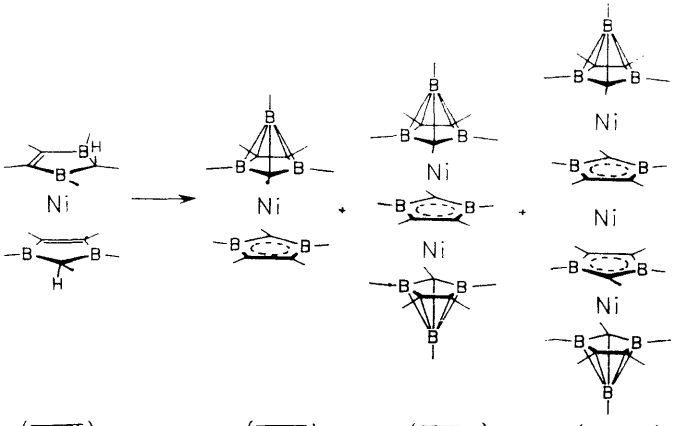
To extend the number of stacks, we have explored routes to pentadecker and hexadecker complexes. The pentadecker *72* was first obtained upon reaction of the tetranuclear complex *71* with the ligand *10*, which replaces the two CO groups of the diamagnetic, 58 VE *71* to yield the paramagnetic, 57 VE *72*. Alternatively, *72* is formed when the allyl groups in the triple-decker *44* is susbtituted for *10* to give the unsymmetrical triple-decker sandwich *45*. Its reaction with *44* leads to the pentadecker *72*.[41] This compound has been studied by X-ray, ESR, paramagnetic NMR and cyclic voltammetry. It was shown that paramagnetic *72* can be reduced to the diamagnetic, 58 VE anion and to the paramagnetic, 59 VE dianion. The next step led us to the synthesis of the first hexadecker sandwich complex via the reaction of the bis(allyl)tetradecker *73* with two sandwich molecules *26* in refluxing mesitylene. Besides the diamagnetic 70 VE hexadecker *74* paramagnetic triple-decker and tetra-decker were also formed.[42] The second route leading to *74* involves stacking at both ends of the bis(2,3-dihydro-1,3-diborole)nickel sandwich *34* with the allyl-triple-decker *44* at 160 °C. Again several by-products are formed, which can be separated by column chromatography. Due to the poor quality of the crystals structural determination of the red-violet *74* was unsuccessful.



(LXXIII) (LXXIV)

V. Carboranyl sandwich complexes

The bis(2,3-dihydro-1,3-diborole)nickel sandwich *34* exhibits an unusual reactivity: at room temperature it is slowly transformed into *75* and a series of carboranyl nickel oligodecker complexes *76*, *77* and higher molecular species (determined by FAB mass spectra up to the decadecker complex).[43]



(XXXIV) (LXXV) (LXXVI) (LXXVII)

Its formation occurs via capping of the diborolyl ring with a boranediyl fragment (R—B:) to give *75* after elimination of the two axial hydrogen atoms from *34*. Besides capping, a stacking to oligodecker takes place, which leads to *76*, *77* and higher oligodeckers. Several of the new carboranylnickel complexes have been structurally characterised.[43,44] This unusual finding of capping and stacking at room temperature clearly indicated a route to polydecker formation. The problem was to prevent the capping reaction, because it stops the one-dimensional system from growing.

VI. Polydecker sandwich complexes

For the synthesis of polydecker compounds reactive monomers and/or dimers are required. Reactions of sandwich complex dianions with metal dications shoud lead to polymers. However, the only complex dianion $[(C_3H_3B_2)_2Pt]^{2-}$ [*36*]$^{2-}$ was oxidised by Fe^{2+} to neutral *36* in an attempt to build a mixed-metal polymer, *78*—*79*.

The unusual reaction sequence of capping and stacking when the nickel sandwich *34* is heated to 80 °C for one hour in benzene to give *75*—*77* and higher oligomers indicated that the combination of Ni(d^{10}) and the 2,3-dihydro-1,3-diborolyl [*10*—H] leads to stacked products. This "self-organisation" of stacks (which also occurs slowly at room temperature) has the disadvantage of the capping reaction (tricarbahexaboranyl formation) and therefore prevents the oligomers from growing to polymers. Therefore we have studied polycondensation reactions of tris(allyl)dinickel-(μ-2,3-dihydro-1,3-diborolyl) complexes *78*, which on heating slowly to 200 °C *in vacuo* yield black polymeric products *79*, bis(allyl)nickel and hexadiene.[5,45] The material is readily attacked by oxygen at ambient temperature. It does not dissolve in toluene, tetrahydrofuran or methylene chloride. A TGA study of three polymeric products with different substituents at the 1,3-diborolyl ring showed that on heating from 200 to 450 °C the polymers lose weight (almost linearly with increasing temperature). Above 450 °C the loss of mass is

reduced (Fig. 2, heating was carried out under an atmosphere of nitrogen, 10 °C/min, up to 600 °C). The absolute mass losses of three polymers (in the range 200–600 °C) amount to 26–27%.

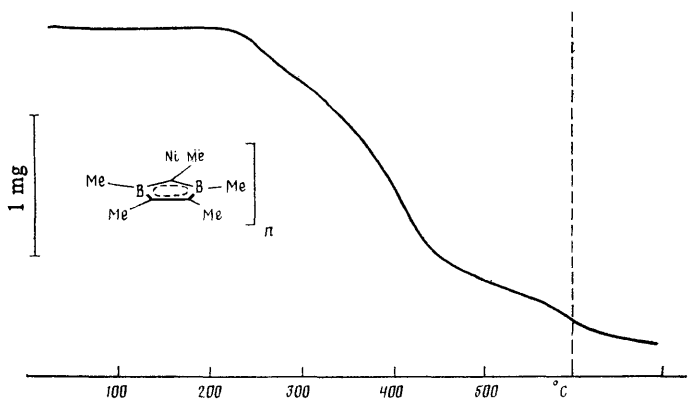
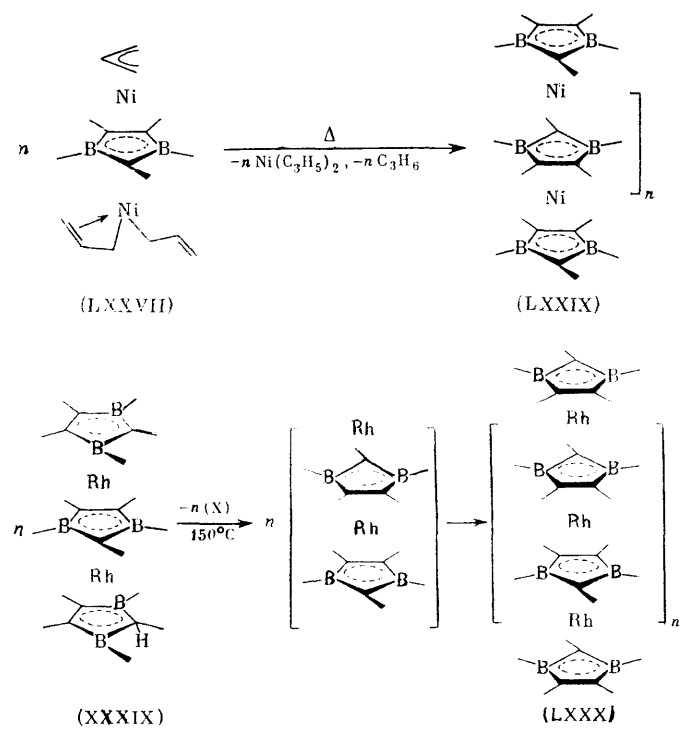


Figure 2. TGA study of compound (LXXIX).

The second polymer was formed by heating the red sandwich *33* to give the green rhodium triple-decker *39*. Elimination of the terminal 2,3-dihydro-1,3-diborole ligand *10* occurs, leaving the reactive double stack behind, which undergoes stacking to the black polymer. *12a* is less sensitive to oxygen than *79*.



The nickel and rhodium polydeckers are amoprhous and insoluble in organic solvents. Therefore a determination of the average molecular weight is not possible. EXAFS studies of *79* at 120, 300 and 340 K confirm the polydecker sandwich structure.[45,46] A 1:1 ratio of Ni to ligand and a Ni...Ni distance of 3.35 Å was observed. Preliminary results of an EXAFS study of the rhodium polymer *80* indicate a Rh...Rh distance of 3.6 Å.

Conductivity measurement on the nickel polymer gave results which are characteristic for a semiconductor (hopping mechanism). The four-probe measurements at room temperature yielded a conductivity of 10^{-2} Scm^{-1} which is similar to that of germanium. In contrast the rhodium polymer is an insulator, the conductivity is 10^{-10} Scm^{-1}. The high sensitivity toward oxygen results in a drop of the conductivity when the sample is exposed to air or doped with iodine. However, chemical alteration of the ligand and the switch to less electronic-rich metals (e.g. iron) may have stabilising effects.

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References

1. J S Miller, A J Epstein *Prog. Inorg. Chem.*, 1976, **20** 1; J R Williams *Adv. Inorg. Chem. Radiochem.*, 1983, **26** 235
2. J A Ibers, L J Pace, J Martinsen, B M Hoffman *Struct. Bonding*, 1982, **50** 1; B M Hoffman, J A Ibers *Acc. Chem. Res.*, 1983, **16** 15
3. J S Miller (Editor) *Extended Linear Chain Compounds*, Plenum Press, New York, 1982, Vol. 1–*3*
4. W Siebert *Angew Chem.*, 1985, **97** 924; *Angew Chem., Int. Ed. Engl.*, 1985, **24** 943
5. W Siebert *Pure Appl. Chem.*, 1988, **60** 1345
6. M C Böhm *Z. Naturforsch. B*, 1984, **39** 223
7. E Schumacher, R Taubenest *Helv. Chim. Acta*, 1964, **47** 1525
8. H Werner, A Salzer *Synth. React. met. Org. Chem.*, 1972, **2** 239; A Salzer, H Werner *Synth. React. Metal-Org. Chem.*, 1972, **2** 249; *Angew. Chem.*, 1982, **84** 949; *Angew. Chem., Int. Ed. Engl.*, 1982, **11** 930
9. A R Kudinov, M I Rybinskaja, Yu T Struchkov, A I Yanovskii *J. Organomet. Chem.*, 1987, **336** 187
10. A W Duff, K Jonas, R Goddard, H-J Kraus, C Krüger *J. Am. Chem. Soc.*, 1983, **105** 5479
11. W M Lamanna *J. Am. Chem. Soc.*, 1986, **108** 2096
12. O J Scherer, J Schwalb, G Wolmershäuser, W Kaim, R Groß *Angew. Chem.*, 1986, **98** 349; O J Scherer, H Sitzmann, G Wolmershäuser *Angew. Chem.*, 1985, **97** 358; O J Scherer, W Wiedemann, G Wolmershäuser *Chem. Ber.*, 1990, **123** 3
13. A L Rheingold, M J Foley, P J Sullivan *J. Am. Chem. Soc.*, 1982, **104** 4727
14. R N Grimes *Coord. Chem. Rev.*, 1979, **28** 47
15. W Siebert *Adv. Organomet. Chem.*, 1980, **18** 301; W Siebert in *Transition Metal Chemistry* (Edited by A Müller, E Diemann), Verlag Chemie, Weinheim 1981, p. 161
16. G E Herberich in G Wilkinson, F G A Strone, F W Abel (Editors) *Comprehensive Organometallic Chemistry*, Pergamon Press, Oxford, 1982, Vol. I, p. 381

17. J W Lauher, M Elian, R H Summerville, R Hoffmann *J. Am. Chem. Soc.*, 1976, **98** 3219
18. P T Chesky, M B Hall *J. Am. Chem. Soc.*, 1984, **106** 5186
19. W Siebert *Pure Appl. Chem.*, 1987, **59** 947
20. R N Grimes *Pure Appl. Chem.*, 1987, **59** 847 and references therein
21. D C Beer, V R Miller, L G Sneddon, R N Grimes, M Mathew, G J Palenik *J. Am. Chem. Soc.*, 1973, **95** 3046
22. J H Davis Jr, E Sinn, R N Grimes *J. Am. Chem. Soc.*, 1989, **11** 4776
23. K Stumpf, W Siebert, R Köster, G Seidel *Z. Naturforsch., B*, 1987, **42** 186
24. V Schäfer, H Pritzkow, W Siebert *Chem. Ber.*, 1989, **122** 401
25. J Edwin, M Bochmann, M C Böhm, D E Brennan, W E Geiger, C Krüger, J Pebler, H Pritzkow, W Siebert, W Swiridoff, H Wadephohl, J Weiss, U Zenneck *J. Am. Chem. Soc.*, 1983, **105** 2582
26. K Geilich, W Siebert *Z. Naturforsch., B*, 1986, **41** 671
27. H Wadepohl, H Pritzkow, W Seibert *Chem. Ber*, 1985, **118** 729
28. M W Whiteley, H Pritzkow, U Zenneck, W Siefert *Angew. Chem., Int. Ed. Engl.*, 1982, **94** 464; *Angew. Chem., Int. Ed. Engl.*, 1982, **21** 453
29. T Kuhlmann, W Siebert *Z. Naturforsch, B*, 1985, **40** 167
30. G E Herberich, B Hessner, W Boveleth, et al. *Angew. Chem.*, 1983, **95** 1024
31. W Siebert, R Full, J Edwin, K Kinberger *Chem. Ber.*, 1978, **111** 823
32. G E Herberich, B Heßner, G Huttner, L Zsolnai *Angew. Chem.*, 1981, **93** 471
33. W Siebert in *Boron Chemistry* (Edited by S Hermànek), World Scientific Publ. Co., Singapore, 1987, p. 476
34. F-F Wörner, W Siebert *Z. Naturforsch., B*, 1989, **44** 1211; K-F Wörner, J-K Uhm, H Pritzkow, W Siebert *Chem. Ber.*, 1990, in the press; J-K Uhm, D Hu, H Pritzkow, W Siebert, H Zenneck *J. Korean. Chem. Soc.*, to be published
35. G E Herberich, B Heßner, M Hostalek *Angew. Chem.*, 1986, **98** 637; *J. Organomet. Chem.*, 1988, **355** 473
36. G E Herberich, H Ohst *J. Organomet. Chem.*, 1986, **307** C16
37. W Siebert, C Böhle, C Krüger, Y-H Tsay *Angew. Chem.*, 1978, **90** 558; *Angew. Chem., Int. Ed. Engl.*, 1978, **17** 527
38. K Jonas *Adv. Organomet. Chem.*, 1981, **19** 97; K Jonas, L Schieferstein *Angew. Chem.*, 1979, **91** 590; *Angew. Chem., Int. Ed. Engl.*, 1979, **18** 549; *Angew. Chem., Int. Ed. Engl.*, 1985, **97** 292 and 1985, **24** 295
39. J Edwin, M C Böhm, N Chester, D M Hoffman, R Hoffmann, H Pritzkow, W Wiebert, K Stumpf, H Wadepohl *Organometallics*, 1983, **2** 1666
40. W Siebert, J Edwin, H Wadepohl, H Pritzkow *Angew. Chem.*, 1982, **94** 148; *Angew. Chem., Int. Ed. Engl.*, 1982, **21** 149
41. T Kuhlmann, Dissertation, Universität Heidelberg, 1985
42. T Kuhlmann, W Siebert *Z. Naturforsch., B*, 1985, **40** 167
43. T Kuhlmann, H Pritzkow, U Zenneck, W Siebert *Angew. Chem.*, 1984, **96** 994; *Angew. Chem., Int. Ed. Engl.*, 1984, **23** 965
44. J Zwecker, T Kuhlmann, H Pritzkow, W Siebert, U Zenneck *Organometallics*, 1988, **7** 2316
45. T Kuhlmann, R Roth, J Rozière, W Siebert, U Zenneck *Synthetic Metals*, 1987, **19** 757
46. T Kuhlmann, S Roth, J Rozière, W Siebert *Angew. Chem.*, 1986, **98** 87; *Angew. Chem., Int. Ed. Engl.*, 1986, **25** 105